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THEORETICAL FREE-ION ENERGIES, DERIVATIVES AND REDUCED MATRIX E--ETC(U)
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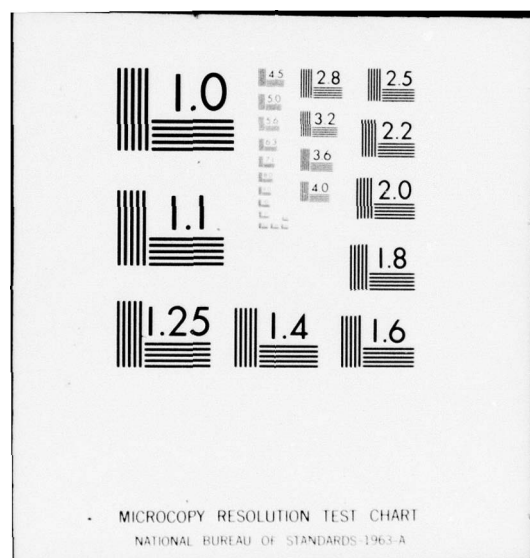
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Theoretical Free-Ion Energies, Derivatives,
and Reduced Matrix Elements

I. Pr^{3+} , Tm^{3+} , Nd^{3+} and Er^{3+}

July 1977



U.S. Army Material Development
and Readiness Command
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Ek, zeta, alpha, beta, and gamma

cont

→ calculate the free-ion centroid energies and derivatives with respect to the E_k , ζ , α , β , and γ of Rajnak and Wybourne's seven-parameter Hamiltonian. Reduced matrix elements for the spherical harmonics in low-lying multiplets of these ions are given.

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1. INTRODUCTION

Much effort in recent years has been devoted to formulating an accurate, yet tractable, theoretical procedure for analyzing the optical spectra of triply ionized lanthanides in crystals. Owing to the many levels in the f^N ground configurations of these ions and to the relatively few low-lying levels whose Stark splittings are observed, it is undesirable and often infeasible to require simultaneous diagonalization of the free-ion Hamiltonian, H , and the crystal field Hamiltonian, H_X . It is preferable first to diagonalize H , the larger interaction, and then to calculate the crystal field splittings by diagonalizing H_X in the low-lying levels. This report examines this procedure, specifically for calculating Pr^{3+} , Tm^{3+} , Nd^{3+} , and Er^{3+} .

Theory cannot yet determine the free-ion Hamiltonian *ab initio*, but its form, $H(P_i)$, is adequately defined by a set of P_i that determine the strengths of the Coulomb, the spin-orbit, and other interactions. Values for these parameters are defined as minimizing the difference between theoretical free-ion centroids evaluated in a basis of intermediate coupled eigenfunctions and experimental free-ion centroids. Since few experimental data are available for the f^N configurations of free, triply ionized lanthanides,¹⁻³ the P_i , in practice, are determined to give a best fit to Stark-level centroids in aqueous solution or in crystals.⁴ Unfortunately, the crystal field affects centroid energies so that, even if all Stark components of a given J-multiplet are determined experimentally, the weighted centroid is not the free-ion energy resulting if the crystal field were "turned off." As a second problem, even the most elaborate free-ion Hamiltonian often cannot give an adequate fit to the J-multiplet centroids once they are determined. The seven-parameter Hamiltonian defined by Rajnak and Wybourne^{5,6} and used extensively by Carnall, Fields, and Rajnak (CFR),⁴ for example, often gives centroid discrepancies of 100 cm^{-1} .

This report describes a method that circumvents the first of these difficulties. The method is based on the fact that, in perturbation theory, changes in wave functions give second-order changes in energy. Conversely, known small changes in energy determine the perturbing Hamiltonian to first order. Thus, any reasonable set of P_i presumably

¹J. Sugar, *Phys. Rev. Lett.*, **14** (1965), 731.

²N. Spector and J. Sugar, *J. Opt. Soc. Am.*, **66** (1976), 436.

³V. Kaufman and J. Sugar, *J. Opt. Soc. Am.*, **66** (1976) 439.

⁴W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49** (1968), 4412-55.

⁵K. Rajnak and B. G. Wybourne, *Phys. Rev.*, **132** (1963), 280.

⁶B. G. Wybourne, *Spectroscopic Properties of Rare Earths*, Interscience Publishers, New York (1965).

determines an adequate set of J-multiplet wave functions and reduced matrix elements, even though the energies they determine, E_j , may be incorrect. An appropriate subset of these "free-ion" J-multiplet wave functions (usually 10 to 15 of the lowest lying) may then be chosen as a basis to calculate Stark splittings, and the energies, E_j^i , of these multiplets may be treated as parameters (along with the crystal field parameters, B_{km} , in H_X) to be varied, as suggested by Margolis,⁷ for obtaining a fit between theoretical and experimental Stark levels.^{8,9} The resultant E_j^i , which, in general, differ (by ΔE_j) from the initial centroids, may finally be used to determine new $P_i' = P_i + \Delta P_i$, as suggested by Wong,¹⁰ by minimizing the function

$$Q = \sum_j \left[\sum_i (\partial E_j / \partial P_i) \Delta P_i - \Delta E_j \right]^2 \quad (1)$$

with respect to ΔP_i . If the ΔP_i determined in this way are not large, then the linearity assumption in Wong's expression is valid, and also it is unnecessary to rediagonalize the free-ion Hamiltonian to determine new reduced matrix elements. These results suggest that it is desirable to perform the initial diagonalization of $H(P_i)$ with P_i that pertain to some convenient host and not to the true free ion since variations in the P_i from host to host are expected to be less than the change in the P_i from the free state to some host.¹¹

Accordingly, we have calculated theoretical energies, derivatives, and reduced matrix elements for the f^2 , f^{12} , f^3 , and f^{11} configurations, respectively, of Pr^{3+} , Tm^{3+} , Nd^{3+} , and Er^{3+} using the aqueous solution free-ion parameters of CFR.⁴ Wong¹⁰ determined the $\partial E_j / \partial P_i$ for Nd^{3+} and Er^{3+} for $P_i = \{E^1, E^2, E^3, \zeta\}$ by a finite differencing method involving five separate diagonalizations for each ion. We have extended and improved on his work by obtaining derivatives also with respect to

⁴W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49** (1968), 4412-55.

⁷J. S. Margolis, *J. Chem. Phys.*, **35** (1961) 1370.

⁸N. Karayianis, D. E. Wortman, and H. P. Jenssen, *J. Phys. Chem. Solids*, **37** (1976), 676.

⁹P. Grunberg, S. Hufner, E. Orlich, and J. Schmidt, *Phys. Rev.*, **184** (1969), 290.

¹⁰E. Y. Wong, *J. Chem. Phys.*, **35** (1961), 544.

¹¹N. Karayianis and C. A. Morrison, *Rare Earth Ion-Host Crystal Interactions. 2. Local Distortion and Other Effects in Reconciling Lattice Sums and Phenomenological B_{km}* , Harry Diamond Laboratories TR-1682 (January 1975), table II.

Rajnak and Wybourne's⁵ higher-order interactions of strengths α , β , and γ and by using Feynman's theorem¹² to obtain derivatives. Feynman's theorem, expressed by

$$\partial E_j / \partial P_i = \langle \psi_j | \partial H / \partial P_i | \psi_j \rangle, \quad (2)$$

where $|\psi_j\rangle$ represents the j th eigenfunction of H , has the advantages of having greater inherent accuracy and of requiring only one diagonalization per ion. To perform the calculations, electrostatic matrices corresponding to the Russell-Saunders basis states given by Nielson and Koster were hand keypunched from their book of tables.¹³ The $V^{(11)}$ and $U^{(k)}$ reduced matrix elements that relate, respectively, to spin-orbit and spherical harmonic reduced matrix elements were calculated from a computer tape containing coefficients of fractional parentage kindly provided by H. M. Crosswhite (Argonne National Laboratory). By choosing to diagonalize H with the aqueous solution parameters of CFR,⁴ we were able to check our computer software procedures by comparing our centroid energies with those of CFR.

A summary of the computational procedures and formulas is given in section 2. Section 3 gives tables of the centroid energies and derivatives and notes some discrepancies between our Nd^{3+} and Er^{3+} energies and those reported by CFR.⁴ Section 4 gives tables of reduced matrix elements of the spherical harmonics and discusses their use in crystal field calculations. Also in section 4, some measure is given of the sensitivity of theoretical Stark levels to the free-ion parameters and wave functions for Nd^{3+} and Er^{3+} in CaWO_4 .

2. CALCULATIONS

To obtain free-ion wave functions, matrix elements of the Hamiltonian

$$H = H_E + H_{SO} + \alpha L^2 + \beta G_2 + \gamma R_7 \quad (3)$$

⁴W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49** (1968), 4412-55.

⁵K. Rajnak and B. G. Wybourne, *Phys. Rev.*, **132** (1963), 280.

¹²E. Merzbacher, *Quantum Mechanics*, John Wiley and Sons, Inc., New York (1961), 396.

¹³C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^N , d^N , and f^N Configurations*, The MIT Press, Cambridge, MA (1963).

were taken in a given J subspace spanned by the basis functions*

$$|JMLS\omega\rangle = \sum_m \langle L(m)S(M-m) | J(M) \rangle |Lm S M-m \omega\rangle, \quad (4)$$

where $\langle j_1(m_1)j_2(m_2) | j(m) \rangle$ is a Clebsch-Gordon coefficient,¹⁴ and the $|LS\omega\rangle$ are the Russell-Saunders states defined in Nielson and Koster.¹³ The additional quantum number ω represents the pairs and triplets of quantum numbers u_1u_2 and $w_1w_2w_3$ given for each state in Nielson and Koster and corresponding, respectively, to the G_2 and R_7 operators.⁶

Since H is a spherical tensor of rank zero in J space, matrix elements of H in a given J subspace are independent of M. If the quantum number M is suppressed, the electrostatic matrix elements are

$$\langle JL'S'\omega' | H_E | JLS\omega \rangle = \delta_{LL'} \delta_{SS'} \langle LS\omega' | H_E | LS\omega \rangle; \quad (5)$$

the spin-orbit matrix elements for N equivalent electrons of orbital angular momentum ℓ are

$$\begin{aligned} \langle JL'S'\omega' | H_{SO} | JLS\omega \rangle &= -\zeta \{ \ell(\ell+1) [\ell] \}^{\frac{1}{2}} \\ &\times W(1S'LJ; SL') (L'S'\omega' | | V^{(11)} | | LS\omega); \end{aligned} \quad (6)$$

and the matrix elements of the last three operators in equation (3) are

$$\langle JL'S'\omega' | h_i | JLS\omega \rangle = \delta_{LL'} \delta_{SS'} \delta_{\omega\omega'} \langle h_i \rangle, \quad (7)$$

where

$$\langle h_{1;2;3} \rangle = \alpha L(L+1); \beta G_2(u_1u_2); \gamma R_7(w_1w_2w_3). \quad (8)$$

*Note the order of L and S in this definition since it does make a difference in the matrix elements.

⁶B. G. Wybourne, *Spectroscopic Properties of Rare Earths*, Interscience Publishers, New York (1965).

¹³C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^N , d^N , and f^N Configurations*, The MIT Press, Cambridge, MA (1963).

¹⁴M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, *The 3-j and 6-j Symbols*, Technology Press, Cambridge, MA (1959).

M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, *The 3-j and 6-j Symbols*, Technology Press, Cambridge, MA (1959). In terms of their tabulated 3-j symbols, $\langle j_1(m_1)j_2(m_2) | j(m) \rangle [j]^{-\frac{1}{2}} = (-)^{-j_1+j_2-m} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix}$.

The symbol $W(abcd;ef)$ in equation (6) is a Racah coefficient¹⁴ and $[x] \equiv 2x + 1$. Values for the electrostatic matrix elements and the $V^{(11)}$ reduced matrix elements are given in Nielson and Koster;¹³ however, we keypunched only the former. A generalized $V^{(\kappa\kappa)}$ defined by

$$\begin{aligned} (L'S'\omega' || V^{(\kappa\kappa)} || LS\omega) &= N\{s(s+1)[s][L][L'][S][S']\}^{\frac{1}{2}} \\ &\times \sum_{\bar{L}\bar{S}} W(L'\bar{L}\kappa\ell; \ell L) W(S'\bar{S}\kappa s; sS) \\ &\times \sum_{\bar{\omega}} F(L'S'\omega'N; \bar{L}\bar{S}\bar{\omega} N-1) F(LS\omega N; \bar{L}\bar{S}\bar{\omega} N-1), \end{aligned} \quad (9)$$

where $s = 1/2$, allows one to calculate a variety of reduced matrix elements once the coefficients of fractional parentage,¹⁵ F , are available. From H. M. Crosswhite's (Argonne National Laboratory) computer tape containing the F for the f^N configurations, we calculated the $V^{(11)}$, as well as the reduced matrix elements of the spherical harmonics, C_k , according to

$$\begin{aligned} (J'L'S'\omega' || \sum_i C_k(i) || JLS\omega) &= \delta_{SS'} \left\{ \frac{[L][J][J']}{s(s+1)[S]} \right\}^{\frac{1}{2}} \\ &\times \langle \ell(0)k(0) | \ell(0) \rangle W(JkSL'; J'L) (L'S\omega' || V^{(0k)} || LS\omega), \quad * \end{aligned} \quad (10)$$

where $\ell = 3$.

These reduced matrix elements are necessary for the crystal field calculations discussed in section 4. The reduced matrix elements, in general, are defined by

$$\langle j'm' | T_{kq} | jm \rangle = \langle j(m)k(q) | j'(m') \rangle [j']^{-\frac{1}{2}} \langle j' || T_k || j \rangle. \quad (11)$$

*This $V^{(0k)}$ is related to the $U^{(k)}$ in Nielson and Koster by $(|| V^{(0k)} ||) = \{s(s+1)[S]\}^{\frac{1}{2}} (|| U^{(k)} ||)$.

¹³C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^N , d^N , and f^N Configurations*, The MIT Press, Cambridge, MA (1963).

¹⁴M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, *The 3-j and 6-j Symbols*, Technology Press, Cambridge, MA (1959). In terms of their tabulated 6-j symbols, $W(abcd;ef) = (-)^{a+b+c+d} \begin{pmatrix} a & b & e \\ d & c & f \end{pmatrix}$.

¹⁵B. R. Judd, *Operator Techniques in Atomic Spectroscopy*, McGraw-Hill Book Co., Inc., New York (1963), 166-192.

Values for the eigenvalues of the G_2 and R_7 operators, $G_2(u_1u_2)$ and $R_7(w_1w_2w_3)$, are given in table I, which is a copy of Wybourne's⁶ tables 2-6 and 2-7.

Taking matrix elements according to equations (5), (6), and (8) between all $|LS\omega\rangle$ states that satisfy $|L-S| \leq J \leq |L+S|$, one may then choose values for E^1 , E^2 , E^3 (in H_E), ζ (in H_{SO}), α , β , and γ and diagonalize the subspace to obtain free-ion wave functions,

$$|J(LS\omega)\rangle = \sum_{\overline{LS\omega}} A_{\overline{LS\omega}} (LS\omega) |\overline{JLS\omega}\rangle \quad (12)$$

The orbital and spin angular momenta, L and S , in $|J(LS\omega)\rangle$ are not good quantum numbers because of mixing by the spin-orbit interaction, and ω is not a good quantum number because of mixing by both the electrostatic and spin-orbit interactions. Thus, the "almost good quantum numbers" $(LS\omega)$ in parentheses represent values in the limit of the off-diagonal parts of H_E and H_{SO} approaching zero. There is such large mixing in many cases, however, that the assignment of $LS\omega$ values to a given free-ion wave function is arbitrary. The method that we have chosen to make assignments is described in section 3.

TABLE I. VALUES OF $G_2(u_1u_2)$ AND $R_7(w_1w_2w_3)$

u_1u_2	$12G_2$	$w_1w_2w_3$	$5R_7$
00	0	000	0
10	6	100	3
11	12	110	5
20	14	111	6
21	21	200	7
22	30	210	9
30	24	211	10
31	32	220	12
40	36	221	13
		222	15

⁶B. G. Wybourne, *Spectroscopic Properties of Rare Earths*, Interscience Publishers, New York (1965).

3. FREE-ION ENERGIES AND DERIVATIVES

Tables II to V give the assignments, energies, and derivatives for each of the free-ion multiplets of Pr^{3+} , Tm^{3+} , Nd^{3+} , and Er^{3+} , respectively. The arbitrariness in assigning a particular term to some highly mixed multiplet was resolved by scanning the matrix of eigenvectors for the largest magnitude coefficient, assigning the row designation of that coefficient to the column eigenvector, eliminating that row and column from further consideration, and repeating the procedure until the final eigenvector was assigned by default. The square of the designating coefficient is printed under the "PCT. PURE" column of these tables and indicates the percentage of the Russell-Saunders designation present in the free-ion eigenfunction. This procedure is not entirely satisfactory (although it results in a unique one-to-one assignment for a given set of free-ion parameters) because a situation may arise where the Russell-Saunders designation is not the largest component present in an eigenvector. The possible occurrence of this situation is for eigenvectors with a PCT. PURE assignment of less than 50 percent. The $^2\text{G}_{9/2}(1)$ level of Er^{3+} (table V) is an example of this occurrence. It contains 24.23 percent of $^4\text{F}_{9/2}$, but, since that designation had already been assigned to the level at $15,136 \text{ cm}^{-1}$ which contains 57.64 percent of $^4\text{F}_{9/2}$, the next largest percentage, 19.06 percent of $^2\text{G}_{9/2}(1)$, was assigned.

The derivatives with respect to α yield an added dividend since $\partial E/\partial \alpha = \langle L^2 \rangle$ according to equations (2) and (3). Thus, the effective orbital angular momentum of an eigenvector given by

$$L_{\text{eff}} = -1/2 + (1/4 + \partial E/\partial \alpha)^{1/2} \quad (13)$$

gives an indication of the L-mixing induced by the spin-orbit interaction. For the $^2\text{G}_{9/2}(1)$ level of Er^{3+} , $L_{\text{eff}} = 4.32$, indicating that good percentages of $\text{H}_{9/2}$ and $\text{I}_{9/2}$ components⁴ also are present.

Table VI gives the free-ion parameters for these ions in aqueous solution determined by CFR.⁴ Our calculated energy levels agree with theirs for Pr^{3+} and Tm^{3+} . For the $^2\text{H}_{11/2}(2)$ level of Nd^{3+} , we get $16,043$ (adding 130 cm^{-1} to our value in table IV to adjust for their ground state) compared with their⁴ listed $16,026 \text{ cm}^{-1}$. In Er^{3+} , we get $47,811$ and $36,572 \text{ cm}^{-1}$ for the $^2\text{H}_{9/2}(1)$ and $^2\text{H}_{9/2}(2)$ levels, respectively (adding 109 cm^{-1} to our values in table V), while they⁴ list $47,822$ and $36,566 \text{ cm}^{-1}$ --differences of 11 and 6 cm^{-1} , respectively.

⁴W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49** (1968), 4412-55.

TABLE II. PRASEODYMIUM AQUEOUS SOLUTION FREE-ION ENERGIES AND DERIVATIVES

PR(III) C.F.R. J. CHEM. PHYS. 49,4412(1968).
 TOTAL NO. OF STATES = 13
 EO = 0.
 ALPHA = 21.255
 E1 = 4548.20
 E2 = 21.937
 E3 = 466.73
 BETA = -799.940
 GAMMA = 1342.900
 Z = 740.8

STATE	ENERGY	PCT. PURE	DE/DEL	DE/DE2	DE/DE3	DE/DZ	DE/DALPHA	DE/DBETA	DE/DGAMMA
3H 4	0.0	97.21	0.05410	-7.03361	-8.85668	-3.52583	29.71342	1.00406	1.01083
3H 5	2077.5	100.00	-0.00000	-0.00000	-9.00000	-0.50000	30.00000	1.00000	1.00000
3H 6	4251.2	99.71	0.00571	0.19984	-8.95432	2.36217	30.03426	1.00048	1.00114
3F 2	4903.6	97.64	0.04674	6.68317	-0.25040	-2.70197	11.85778	0.15568	1.00935
3F 3	6295.4	100.00	-0.00000	-0.00000	-0.00000	-0.50000	12.00000	0.50000	1.00000
3F 4	6728.3	63.69	0.69619	-90.50445	-1.52789	-0.62869	15.05583	0.73959	1.13924
1G 4	9639.9	62.49	1.24971	-162.46244	-2.61548	2.63451	17.23096	0.92302	1.24984
1D 2	16595.0	89.64	1.79287	256.38028	-7.19113	-0.44908	5.81241	1.13807	1.35857
3P 0	20460.8	99.03	0.08721	-0.00000	32.68023	-1.66900	1.98062	0.99031	0.99031
3P 1	21085.0	100.00	-0.00000	-0.00000	33.00000	-0.50000	2.00000	1.00000	1.00000
11 6	21255.0	99.71	1.99429	69.80016	6.95432	0.13783	41.96574	1.16619	1.39886
3P 2	22290.0	91.89	0.16040	22.93656	29.44452	1.65105	2.32981	1.01292	1.03208
1S 0	46655.5	99.03	8.91279	0.00000	0.31977	0.66900	0.01938	0.00969	0.00969

TABLE III. THULIUM AQUEOUS SOLUTION FREE-ION ENERGIES AND DERIVATIVES

TM(III) C.F.R. J. CHEM. PHYS. 49,4412(1968).
 TOTAL NO. OF STATES = 13
 EO = 0.
 ALPHA = 14.677
 E1 = 7142.40
 E2 = 33.795
 E3 = 674.27
 BETA = -631.790
 GAMMA = 0.000
 Z = 2628.7

STATE	ENERGY	PCT. PURE	DE/DEL	DE/DE2	DE/DE3	DE/DZ	DE/DALPHA	DE/DBETA	DE/DGAMMA
3H 6	0.0	99.13	0.01738	0.60841	-8.86093	-2.70564	30.10430	1.00145	1.00348
3F 4	5609.5	62.66	0.58561	-76.12922	-1.89625	-2.89354	15.79252	0.73548	1.11712
3H 5	8187.6	100.00	-0.00000	-0.00000	-9.00000	0.50000	30.00000	1.00000	1.00000
3H 6	12518.3	59.62	0.25937	-33.79663	-5.88552	1.08381	23.77103	0.88475	1.05199
3F 3	14307.7	100.00	-0.00000	-0.00000	-0.00000	0.50000	12.00000	0.50000	1.00000
3F 2	14914.4	77.36	0.41537	59.39758	-1.66538	-0.69071	10.56628	0.64784	1.08307
1G 4	21172.4	57.72	1.15442	-150.07444	-5.21824	3.31573	22.43650	1.04644	1.23089
1D 2	27829.8	41.15	0.82300	117.68943	8.75990	-0.20123	5.50551	0.97567	1.16466
11 6	34684.3	99.13	1.98262	69.39159	6.86093	0.20564	41.89570	1.16522	1.39652
3P 0	35435.0	95.51	0.40444	0.00000	31.51704	-2.48024	1.91012	0.95506	0.95506
3P 1	36095.9	100.00	-0.00000	-0.00000	33.00000	0.50000	2.00000	1.00000	1.00000
3P 2	37991.1	57.87	0.76172	108.92606	14.90886	2.3207	3.92878	1.04327	1.15240
1S 0	79390.0	95.51	8.59556	0.00000	1.48296	1.48024	0.08988	0.04494	0.04494

TABLE IV. NEODYMIUM AQUEOUS SOLUTION FREE-ION ENERGIES AND DERIVATIVES

ND(AQ) C.F.R. J. CHEM. PHYS. 49,4412(1968).									
TOTAL NO. OF STATES = 41									
E1 = 4739.30 E2 = 23.999 E3 = 485.96									
ALPHA = 0.561 BETA = -117.150 GAMMA = 1321.300									
Z = 884.6									
PAGE 1									
STATE	ENERGY	PCT. PURE	DE/DE1	DE/DE2	DE/DE3	DE/DZ	DE/DALPHA	DE/DBETA	DE/DGAMMA
41 9/2	0.0	96.97	0.09114	-4.29103	-20.99855	-4.36279	41.63605	1.18203	1.21843
4111/2	1876.2	98.96	0.03125	-1.55396	-20.99044	-1.98187	41.88032	1.17175	1.20636
4113/2	3874.1	99.53	0.01405	-0.57561	-20.94561	0.32365	42.05801	1.16908	1.20281
4115/2	5950.0	98.62	0.04149	-1.84741	-20.86103	2.50386	42.19496	1.17473	1.20830
4F 3/2	11396.2	94.15	0.16694	4.21498	-0.76517	-3.32381	11.61840	0.53713	1.23339
4F 5/2	12443.2	97.60	0.07616	-0.51529	-0.75526	-1.79769	11.87429	0.51625	1.21319
2H 9/2 2	12607.8	54.97	2.46688	-14.55631	-14.78460	-3.08354	25.75217	1.43045	1.69347
4S 3/2	13329.4	94.35	0.15193	-0.12750	-0.54319	-1.10892	0.17725	0.05401	1.23039
4S 5/2	13434.4	93.20	0.20708	-15.45790	-0.57949	-0.80360	12.52653	0.56039	1.23923
4F 9/2	14724.1	75.55	0.71200	-35.00387	-4.84186	0.69275	16.22010	0.77437	1.34242
2H11/2 2	15912.9	79.80	2.79546	-148.78510	-18.25352	0.80881	29.56770	1.61035	1.75909
4G 5/2	17036.6	98.51	0.08486	1.32322	11.65913	-3.12142	19.87890	1.16554	1.75909
2G 7/2 1	17203.5	30.82	1.62063	-140.84831	0.62506	-1.71073	19.63062	1.27085	1.52344
2K13/2	18886.7	98.55	2.98680	-133.34713	-10.90300	-1.36786	55.79751	1.74156	1.79737
4G 7/2	18972.6	57.87	1.21778	-96.11825	3.37477	-0.15158	19.79250	1.24289	1.43146
4G 9/2	19414.0	76.12	0.62397	-51.71769	6.82151	0.59431	20.54267	1.21599	1.32482
2K15/2	20885.6	93.90	0.25943	-121.77497	-10.75584	0.65169	56.57185	1.74215	1.79192
2G 9/2 1	21041.5	39.32	2.12189	-160.63677	-4.53805	3.16336	19.93647	1.29618	1.62453
2D 3/2 1	21137.0	45.82	2.72418	-8.52227	-9.57206	-1.97978	4.25055	1.03321	1.74484
4G11/2	21433.2	92.43	0.22634	-18.22842	10.51101	2.18532	20.76216	1.17635	1.24528
2P 1/2	23009.6	93.69	2.81076	0.00000	-8.22450	-0.86339	2.25232	1.01051	1.76215
2D 5/2 1	23735.2	97.29	2.93988	-171.59575	-11.86278	0.40755	6.13558	1.15516	1.78659
2P 3/2	26129.6	48.44	2.87497	26.78931	-11.06838	3.14310	4.06653	1.07143	1.77500
4D 3/2	28181.8	81.60	0.55074	-6.17097	28.45245	-2.18455	5.91728	1.25248	1.31016
4D 5/2	28346.2	79.97	0.66633	40.41976	25.92228	-2.48234	6.15196	1.26818	1.30601
2111/2	28493.6	86.18	2.98553	-6.74711	2.73349	-1.49442	40.30040	1.15279	1.79712
4D 1/2	28762.8	93.69	0.18924	0.00060	30.22450	-0.63661	5.74768	1.15615	1.23785
2115/2	29129.8	95.24	2.99924	93.62158	-3.38354	-0.15553	71.23685	1.74989	1.79988
2113/2	29836.0	98.94	2.99919	-31.07836	2.84855	0.54420	42.14514	1.17271	1.79985
4D 7/2	30423.5	98.47	0.10761	0.91471	32.26028	0.59926	6.09647	1.16254	1.19477
2117/2	30610.1	100.00	3.00000	105.00000	-3.00000	1.00000	72.00000	1.75000	1.80000
2H 9/2 1	32437.3	86.90	2.98685	162.83301	0.21077	-0.25940	29.84859	1.09559	1.79738
2D 3/2 2	33351.0	80.56	2.53129	5.77012	12.48684	0.95398	5.97009	1.63510	1.70626
2H11/2 1	33783.0	69.99	2.96173	166.32450	-1.00209	1.98218	31.49684	1.13899	1.79246
2D 5/2 2	34343.6	59.25	2.88385	160.07582	3.88121	0.89793	7.28120	1.53206	1.58550
2F 5/2 2	38374.0	43.10	4.90492	121.46020	-6.23233	1.47740	10.68417	1.33173	1.39905
2F 7/2 2	39796.4	63.10	4.97722	124.60345	-4.77757	1.74065	12.00387	1.30336	1.37654
2G 9/2 2	47566.2	58.27	2.99837	126.14798	33.13291	-0.24518	20.08042	1.50621	1.79990
2G 7/2 2	48455.7	58.44	3.00595	124.36318	33.66917	0.47261	19.89861	1.51346	1.79828
2F 7/2 1	66128.5	64.17	6.84479	68.82845	38.43763	-0.14678	12.05993	0.94517	1.02911
2F 5/2 1	67444.0	57.44	6.44559	82.96251	41.84739	1.11873	11.99918	1.03186	1.11065

TABLE V. ERBIUM AQUEOUS SOLUTION FREE-ION ENERGIES AND DERIVATIVES

ER(AQ) C.F.R. J. CHEM. PHYS. 49,4412(1968). TOTAL NO. OF STATES = 41 EO = 0. ALPHA = 0. E1 = 6769.90 BETA = -509.280 E2 = 32.388 GAMMA = 646.62 Z = 2380.7									
STATE	ENERGY	PCT. PURE	DE/DE1	DE/DE2	DE/DE3	DE/DZ	DE/DALPHA	DE/DBETA	DE/DGAMMA
4115/2	0.0	97.07	0.08785	-3.88113	-20.70475	-3.62714	42.61479	1.18375	1.21757
4113/2	6500.7	99.10	0.02697	-1.10775	-20.89597	-0.70623	42.11174	1.17132	1.20539
4111/2	10110.7	82.22	0.49381	-18.67994	-20.62226	-0.34327	39.78232	1.25134	1.29881
41 9/2	12271.7	50.53	1.04906	-72.12450	-15.87085	-1.56092	32.08203	1.19633	1.40995
4F 9/2	15136.2	57.64	0.40105	-28.90585	-7.22022	-1.18139	21.68765	0.81434	1.28023
4S 3/2	18352.7	68.41	0.78207	-14.24900	-2.06483	-2.72513	1.48610	0.30289	1.35660
2M11/2 2	19149.1	46.81	1.47848	-41.84595	-10.05236	-1.62794	28.28258	1.43615	1.49571
4F 7/2	20312.9	92.33	0.23943	-15.62487	-0.69610	-0.70969	12.57284	0.56629	1.24303
4F 5/2	21765.4	84.62	0.46095	24.77997	-2.31164	-0.73912	11.13845	0.61452	1.28814
4F 3/2	22312.7	62.57	0.62567	-24.47200	-1.03900	-0.74972	8.74190	0.55543	1.32515
2G 9/2 1	24400.0	19.06	1.71019	-143.01340	-7.95987	0.49886	23.02365	1.17476	1.54216
4G 9/2	26391.1	60.29	1.11390	-80.34100	0.66591	-0.11431	24.28932	1.30324	1.42286
2K15/2	27691.4	79.02	0.47786	-17.48787	4.99170	0.11151	22.57431	1.25178	1.29566
2K15/2 1	27872.0	26.18	2.91417	-117.33655	-10.82793	-1.31691	56.52323	1.73341	1.78294
2S 7/2 1	31542.5	21.61	1.74479	-135.94285	1.20751	-0.66486	19.30577	1.27834	1.50880
2D 3/2 1	32376.2	89.66	1.82695	-88.14168	-0.35396	0.41133	5.31445	0.83036	1.56549
2K13/2	32976.2	92.02	0.98312	-123.97877	-9.58801	3.48942	54.55301	1.68971	1.79662
4G 5/2	33279.3	91.62	0.37923	-1.54856	10.91779	-1.07898	19.23514	1.17448	1.74974
2P 1/2	33343.4	91.62	2.74871	0.00000	-7.31440	-0.75041	2.33505	1.01396	1.45452
4G 7/2	33914.1	54.44	1.29728	-97.27944	2.49634	2.27004	19.74714	1.23726	1.63389
2D 5/2 1	34693.4	57.46	2.17374	177.74144	-9.29904	-0.39853	6.84208	1.16250	1.40582
2H 9/2 2	34693.0	32.00	2.39863	-176.51601	-10.10773	4.64662	24.63837	1.40582	1.67973
4D 5/2	34664.5	44.83	1.57733	-191.59273	24.32960	-1.16418	6.37021	1.30345	1.51305
4D 7/2	35048.3	95.42	0.25154	1.63166	31.06315	-1.54718	6.36446	1.15441	1.19105
2L11/2	40898.2	66.21	2.95808	18.66149	2.40092	-1.37998	37.83027	1.12636	1.79167
2L17/2	41576.9	100.00	3.00000	105.00000	-3.00000	-1.00000	72.00000	1.75000	1.80000
4D 3/2	42148.9	58.06	1.07853	45.92002	13.56552	1.49007	6.03074	1.13291	1.41572
2P 3/2	42854.6	36.60	2.36065	-143.43999	9.51311	1.77545	4.44192	1.20675	1.67215
2I13/2	43607.9	90.13	2.98990	-39.91349	1.58398	0.71681	43.33526	1.22230	1.79798
4D 1/2	46931.0	91.62	0.25129	0.00000	29.31440	2.25041	5.66495	1.15271	1.25026
2H 9/2 1	47702.4	76.92	2.97435	199.68165	-0.94173	0.00194	29.50156	1.16390	1.79491
2D 5/2 2	47806.9	94.23	2.99850	91.21539	-3.46858	1.94410	71.07326	1.74981	1.79981
2M11/2 1	50891.3	55.41	1.98825	53.25441	15.25086	1.22846	7.04350	1.45834	1.50898
2F 7/2 2	50951.0	56.22	2.95604	113.19905	0.40630	2.16558	33.82158	1.13314	1.79123
2F 3/2 2	50917.5	68.98	4.85388	113.13661	-4.06826	0.19722	12.15308	1.25821	1.34152
2F 5/2 2	51279.6	64.43	2.32658	263.40402	-0.62083	4.29822	5.98663	1.55528	1.66543
2S 7/2 2	53129.0	57.33	3.82913	127.60442	4.97369	3.70205	11.37402	1.49909	1.56102
2S 9/2 2	53329.0	56.19	3.00102	125.29858	33.75629	-0.93645	19.74601	1.51850	1.79801
2F 5/2 1	63492.4	76.73	2.98956	130.34027	32.11037	1.22013	20.30316	1.49359	1.79801
2F 7/2 1	71217.3	60.45	7.59200	44.04087	31.14574	-0.20731	12.00050	0.78812	0.87686
			6.61331	74.76657	39.78626	1.38489	12.11965	0.98764	1.07187

TABLE VI. FREE-ION PARAMETERS FOR TRIPLY IONIZED Pr, Nd, Er, AND Tm

Ion	E ¹	E ²	E ³	ζ	α	B	γ
Pr ^a	4548.2	21.937	466.73	740.75	21.255	-799.94	1342.9
Nd ^a	4739.3	23.999	485.96	884.58	0.5611	-117.15	1321.3
Nd ^b	4676.4	23.764	480.25	877.25	0.336	-112.52	1241.3
Nd ^c	4988.0	24.510	493.90	906.00	0.0	0.0	0.0
Er ^a	6769.9	32.388	646.62	2380.7	18.347	-509.28	649.71
Er ^b	6632.0	31.128	652.18	2399.7	23.137	-626.04	883.04
Tm ^a	7142.4	33.795	674.27	2628.7	14.677	-631.79	0.0

^aFor aqueous solution. See T. Carnall et al, J. Chem. Phys., 49 (1968), 4412-55.

^bFor CaWO₄.

^cFor LaCl₃. See E. Y. Wong, J. Chem. Phys., 35 (1961), 544.

Eight other levels differ in energy from 2 to 4 cm⁻¹ in Er³⁺. We do not know the source of these discrepancies, and we solicit results from an independent calculation. One further contact was made with Wong's Nd³⁺ calculations¹⁰ where we found agreement to 0.6 cm⁻¹ except for his ⁴G_{7/2} level at 19,288.93 cm⁻¹. We calculate this energy as 19,228.9 cm⁻¹, strongly indicating a misprint in Wong's table that would be easy to miss in proofreading. We also agree with his $\partial E/\partial \zeta$ calculations for all his levels with spot checks with his $\partial E/\partial F_k$ values, converting them to our $\partial E/\partial E^k$.

4. Nd AND Er IN CaWO₄

Using the procedure described in section 1, we determined¹⁶ free-ion centroids for Nd³⁺ and Er³⁺ and crystal field parameters in CaWO₄ by fitting, respectively, to 51 (of 64) and 38 (of 48) identified experimental Stark levels. The Nd³⁺ centroids for the lowest 14 multiplets* were fit by using the derivatives of table IV to determine

*Actually, the ²K_{13/2} multiplet is lower than the ⁴G_{7/2} multiplet that was the highest multiplet diagonalized (see table IV). However, the number of Stark levels in ²K_{13/2} exceeded the available core capacity in the IBM 7094 computer used to perform these calculations, so the ⁴G_{7/2} multiplet was used instead.

¹⁰E. Y. Wong, J. Chem. Phys., 35 (1961), 544.

¹⁶Donald E. Wortman, Clyde A. Morrison, and Nick Karayianis, Rare Earth Ion-Host Lattice Interactions. 5. Lanthanides in CaWO₄, Harry Diamond Laboratories TR-1794 (June 1977).

the free-ion parameters for CaWO_4 given in table VI, line 3. Table VII gives theoretical centroids by using aqueous parameters, theoretical centroids by using CaWO_4 parameters, and experimental centroids for comparison. The listed centroids corresponding to CaWO_4 parameters were obtained by Wong's procedure by using our derivatives, yet they differ only by 0.27 cm^{-1} rms from the exact values obtained by rediagonalizing the free-ion matrices. The new eigenfunctions and reduced matrix elements obtained by rediagonalizing were then used to recalculate the

TABLE VII. Nd^{3+} MULTIPLY CENTROIDS (cm^{-1})

Multiplet	Carnall parameters ^a	Best fit parameters ^b	Experimental ^c (CaWO_4 centroids)
$^4I_{9/2}$	84	219	222
$^4I_{11/2}$	1961	2081	2089
$^4I_{13/2}$	3958	4063	4066
$^4I_{15/2}$	6034	6120	6117
$^4F_{3/2}$	11481	11488	11453
$^4F_{5/2}$	12528	12528	12503
$^2H_{9/2}(2)$	12692	12632	12597
$^4S_{3/2}$	13414	13406	13447
$^4F_{7/2}$	13519	13507	13539
$^4F_{9/2}$	14808	14775	14721
$^2H_{11/2}(2)$	15997	15903	15947
$^4G_{5/2}$	17121	17065	17102
$^2G_{7/2}$	17288	17196	17228
$^4G_{7/2}$	19057	18959	18910
rms deviation (cm^{-1})	85.14	33.34	

^aCalculated by using parameters of W. T. Carnall, P. R. Fields, and K. Rajnak (CFR) [J. Chem. Phys., **49** (1968), 4412-55], table VI, line 2, and centered to experimental centroids.

^bCalculated by using derivatives of centroids with respect to CFR parameters to fit CaWO_4 centroids. Exact centroids by using parameters table VI, line 3, differ from these by an rms of 0.27 cm^{-1} .

^cDonald E. Wortman, Clyde A. Morrison, and Nick Karayianis, Harry Diamond Laboratories TR-1794 (June 1977).

Stark splittings for $\text{Nd}^{3+}:\text{CaWO}_4$ by using the crystal field parameters determined by the original fitting procedure. Deviations between the theoretical energy levels of the two calculations were 1.8 cm^{-1} or less for the lowest 53 Stark levels and 1.94 rms for the highest 11 levels shown in table VIII. This exercise indicates, fortunately, that the aqueous eigenvectors and reduced matrix elements are adequate for Nd^{3+} crystal field calculations at least to the degree of accuracy obtainable by the seven-parameter free-ion Hamiltonian considered here. Because of the inability of this theory, however, to obtain a better fit to free-ion centroids, one cannot at this stage predict the effects on crystal field calculations of a more profound free-ion theory.

TABLE VIII. EFFECT OF Nd^{3+} FREE-ION WAVE FUNCTIONS ON THEORETICAL STARK LEVELS FOR THREE EXCITED MULTIPLETS

Multiplet	Stark energies for CaWO_4 (cm^{-1})			
	2μ	Theoretical ^a	Theoretical ^b	$ \Delta $
${}^4\text{G}_{5/2}$	3	16979.7	16980.9	1.2
(17101.8)	1	17041.3	17041.9	0.6
	3	17098.0	17100.6	2.6
${}^2\text{G}_{7/2}(1)$	1	17223.1	17225.5	2.4
(17227.9)	3	17251.5	17249.7	1.8
	1	17303.2	17300.2	3.0
	3	17426.6	17423.1	3.5
${}^4\text{G}_{7/2}$	1	18809.0	18808.2	0.8
(18911.1)	3	18903.3	18904.5	1.2
	3	18993.7	18993.9	0.2
	1	19013.3	19014.1	0.8
				rms 1.94

^aFree-ion wave functions by using aqueous parameters of W. T. Carnall, P. R. Fields, and K. Rajnak (CFR) [J. Chem. Phys., 49 (1968), 4412-55], table VI, line 2, and CaWO_4 crystal field parameters $B_{20} = 496.662$; $B_{40} = -867.308$; $B_{44} = 1032.75$; $B_{60} = -8.09$; and $B_{64} = 900.433 + i255.00 \text{ cm}^{-1}$.

^bFree-ion wave functions by using CaWO_4 parameters (table VI, line 3) and crystal field parameters given above.

In connection with the best-fit free-ion parameters for $\text{Nd}^{3+}:\text{CaWO}_4$ (table VI, line 3), they are the best-fit parameters only to within certain limitations imposed on their deviation from the aqueous parameters. The rigorous, best-fit parameters gave a fit to 28.23 cm^{-1} (instead of the 33.34 cm^{-1} fit obtained with the above parameters), but deviated wildly from the aqueous values, for example, α , β , and $\gamma = -40.47$, 727.92 , and $-13,284.7$, respectively. These deviations were pared to deviations compatible with the parameter fluctuations that CFR^4 found over the lanthanide series and then were held constant while best fits with the E^k and ζ were obtained. The result of this exercise, though somewhat arbitrary, was nevertheless physically palatable and was sufficient for performing the tests on the theory described above.

Table IX shows the improved free-ion centroid fit obtained for the lowest 10 multiplets of $\text{Er}^{3+}:\text{CaWO}_4$ by varying the free-ion parameters. Similar restrictions on α , β , and γ to those described above were imposed and resulted in the CaWO_4 parameters given in table VI, line 6. Perhaps a more liberal leeway on the α , β , and γ deviations should have been allowed in this fit because, whereas the rigorous, best fit parameters gave a fit to 3.32 cm^{-1} , the constrained parameters gave a fit only to 47.73 cm^{-1} . Nevertheless, the CaWO_4 free-ion parameters obtained with the constraint differ sufficiently from the aqueous parameters of CFR^4 to perform a test of the theory similar to that for Nd described above.

In the 48 Stark-split levels in the 10 lowest multiplets of Er^{3+} in CaWO_4 calculated by the two sets of free-ion wave functions, theoretical differences were only 1.13 cm^{-1} rms, even less than differences found in Nd^{3+} . This calculation gives further strong evidence of the insensitivity of crystal field calculations to free-ion parameter changes between host materials.

As a result of these exercises, we conclude that, within the limitations of the seven-parameter free-ion Hamiltonian, the reduced matrix elements for the C_{km} in the crystal field Hamiltonian

$$H_x = \sum_{km} B_{km} \sum_i C_{km}(i) \quad (14)$$

⁴W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49** (1968), 4412-55.

TABLE IX. Er^{3+} MULTIPLET CENTROIDS (cm^{-1})

Multiplet	Carnall parameters ^a	Best fit parameters ^b	Experimental ^c (CaWO_4 centroids)
$^4I_{15/2}$	144	124	155
$^4I_{13/2}$	6645	6681	6632
$^4I_{11/2}$	10255	10258	10241
$^4I_{9/2}$	12416	12409	12489
$^4F_{9/2}$	15280	15324	15297
$^4S_{3/2}$	18497	18454	18403
$^2H_{11/2}(2)$	19293	19190	19146
$^4F_{7/2}$	20457	20532	20519
$^4F_{5/2}$	22109	22092	22178
$^4F_{3/2}$	22457	22489	22492
rms deviation (cm^{-1})	68.10	47.73	

^aCalculated by using parameters of W. T. Carnall, P. R. Fields, and K. Rajnak (CFR) [J. Chem. Phys., 49 (1968), 4412-55], table VI, line 5, and centered to experimental centroids.

^bCalculated by using derivatives of centroids with respect to CFR parameters to fit CaWO_4 centroids. Exact centroids by using parameters of table VI, line 6, differ from these by an rms of 3.42 cm^{-1} .

^cDonald E. Wortman, Clyde A. Morrison, and Nick Karayianis, Harry Diamond Laboratories TR-1794 (June 1977).

evaluated in the aqueous free-ion basis wave functions may be used independently of host. These reduced matrix elements are given for Pr^{3+} , Tm^{3+} , Nd^{3+} , and Er^{3+} for $k = 2, 4, 6$ in tables X to XXI. These tables give $\langle J'(L'S'\omega') | \sum_i C_k(i) | J(LS\omega) \rangle$,* where a general crystal field matrix element is evaluated according to

$$\begin{aligned} \langle J'M'(L'S'\omega') | \sum_i C_k(i) | JM(LS\omega) \rangle &= \langle J(M)k(m) | J'(M') \rangle \\ &\times [J']^{-1/2} \langle J'(L'S'\omega') | \sum_i C_k(i) | J(LS\omega) \rangle. \end{aligned} \quad (15)$$

*Multiply these reduced matrix elements, respectively, by $-\sqrt{15/28}$, $\sqrt{22/28}$, and $-\sqrt{429/700}$ --values of $\langle 3(0)k(0) | 3(0)\sqrt{7} \rangle^{-1}$ --for $k = 2, 4$, and 6 to obtain the reduced matrix elements $\langle |U^{(k)}| \rangle$.

TABLE X. Pr^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S')||\Sigma C_2||J(LS))$

n'	$\psi_{n'}$	n'_0	$(\psi_{n'} \Sigma C_2 \psi_n)$						
			n_0	n_0+1	n_0+2	n_0+3	n_0+4	n_0+5	n_0+6
1	3P 0	4	0.596362	-0.742609	-0.165856				
2	1S 0	4	-0.352898	-0.085191	-0.966218				
3	3P 1	3	-0.547722	-0.887462	-0.708172	0.379780	-1.032794		
4	3P 2	4	0.855283	-0.244479	0.045818	-0.693723	-0.878429	0.009562	-1.121449
5	3F 2	5	0.339609	0.159808	-0.197953	0.052284	-0.974662	-0.008547	
6	1D 2	6	0.836994	0.239456	1.061070	-0.070405	-0.744106		
7	3F 3	7	0.341565	-0.216014	-0.349532	-0.088500	-1.083203		
8	3F 4	8	0.158500	-0.186944	0.385431	-0.233227	-1.021430	0.414422	
9	3H 4	9	-1.205814	0.047739	0.452078	-0.014099	-0.131521		
10	1G 4	10	-0.028045	-0.268138	-0.705772	-0.666234			
11	3H 5	11	-1.309959	0.449048	0.024027				
12	3H 6	12	-1.520235	0.080881					
13	1I 6	13	-3.027486						

The (LS_w) are the assigned Russell-Saunders designations for the free-ion wave functions according to the discussion in section 3. To save space and avoid printing reduced matrix elements that are identically zero because the triangle condition among J , k , and J' is not met, column 3 in each of these tables gives the number of the first multiplet (n) to which the multiplet in column 2 connects. Across a row, the reduced matrix elements correspond to $(\psi_{n'}||\Sigma C_k||\psi_n)$ as n increases in steps of unity from the value n listed in column 3. The lower half of the matrix of reduced matrix elements is given by

$$(J||\Sigma C_k||J') = (-)^{J'-J} (J'||\Sigma C_k||J) . \quad (16)$$

With these tables, one does not need to know the specific structure of an individual free-ion wave function. One may (1) take all or any particular subspace of the multiplets; (2) set up crystal subspaces of states with given M that are connected by H_x ; (3) evaluate the interaction matrix according to equation (15) and the centroid energy parameters $E(J(LS_w))$, where

TABLE XI. Pr^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S')) || \Sigma C_n || J(LS))$

n'	$i_{n'}$	n_0	$n =$									
			n_0	n_0+1	n_0+2	n_0+3	n_0+4	n_0+5	n_0+6	n_0+7	n_0+8	n_0+9
1	3P 0	8	-0.369012	0.468868	-0.266779							
2	1S 0	8	-0.469102	0.094570	0.703800							
3	3P 1	7	0.499999	0.575542	0.466072	0.332594	0.603022					
4	3P 2	4	0.103524	-0.615506	0.306743	-0.626231	-0.361316	0.214782	-0.246944	0.490479	0.797834	0.181261
5	3F 2	5	-0.091695	0.327554	0.254669	-0.039648	0.716362	-0.142251	-0.615599	0.144726	0.082544	
6	1D 2	6	0.652185	0.146191	-0.002803	-0.147208	0.253955	-0.047313	-0.289576	0.447794		
7	3F 3	7	-0.062675	0.303376	0.664463	0.088177	0.664346	-0.636433	-0.034054			
8	3F 4	8	-0.564849	0.252328	0.432757	0.625681	0.874445	-0.912684				
9	3H 4	9	-0.768412	0.095408	0.506674	-0.204849	0.256516					
10	1G 4	10	-0.911851	0.361568	0.585520	1.316835						
11	3H 5	11	-0.683293	0.544301	0.029124							
12	3H 6	12	-0.951463	-0.127825								
13	1I 6	13	1.430614									

TABLE XII. Pr^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S')) || \Sigma C_6 || J(LS))$

n'	$\varphi_{n'}$	n_o	$(\varphi_{n'} \Sigma C_6 \varphi_n)$						
			n_o	n_o+1	n_o+2	n_o+3	n_o+4	n_o+5	n_o+6
1	3P 0	12	0.344329	-0.076765					
2	1S 0	12	0.017784	-0.961341					
3	3P 1	11	-0.381690	-0.450976	-0.024131				
4	3P 2	8	0.129430	0.470155	-0.166139	0.464251	0.296966	-0.482656	
5	3F 2	8	0.382606	0.438258	0.105357	-1.037022	0.703888	-0.231448	
6	1D 2	8	0.186369	-0.291352	-0.351648	0.028572	-0.103263	-1.672322	
7	3F 3	7	-0.319345	-0.092953	1.067449	-0.291482	0.000000	-1.174953	-0.062869
8	3F 4	8	-0.258766	0.889523	0.763671	0.841322	0.862787	0.846305	
9	3H 4	9	0.658622	0.208546	-0.998429	0.477071	-0.197532		
10	1G 4	10	-1.003319	0.835684	0.636235	-1.037987			
11	3H 5	11	0.445123	-1.023579	-0.054769				
12	3H 6	12	1.134016	0.085047					
13	1I 6	13	-0.450876						

TABLE XIII. Tm^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S')) || \Sigma C_2 || J(LS))$

n'	$\varphi_{n'}$	n_o	$(\varphi_{n'} \Sigma C_2 \varphi_n)$						
			n_o	n_o+1	n_o+2	n_o+3	n_o+4	n_o+5	n_o+6
1	3P 0	4	-0.478731	0.812148	-0.224881				
2	1S 0	4	-0.756045	-0.305446	0.629148				
3	3P 1	3	0.547722	0.574662	0.512364	0.916868	1.032794		
4	3P 2	4	-0.915430	0.089385	0.026101	0.513104	0.493808	0.713875	-1.064602
5	3F 2	5	-0.510792	0.345813	0.085387	-0.747708	0.744068	0.109043	
6	1D 2	6	-0.605753	0.554295	1.036016	0.487717	0.586714		
7	3F 3	7	-0.341565	0.067844	0.391384	0.137411	1.083203		
8	3F 4	8	-0.135608	-0.491240	0.081259	0.412849	1.001638	0.337688	
9	3H 4	9	0.706724	0.540142	-0.156614	0.665526	-0.349806		
10	1G 4	10	0.504239	-0.368366	-0.300152	0.633915			
11	3H 5	11	1.309959	-0.447732	0.041924				
12	3H 6	12	1.529082	0.140710					
13	1I 6	13	3.018638						

TABLE XIV. Tm^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S')) || \Sigma C_n || J(LS))$

n'	$J' L' S'$	n_0	$(\tau_n \Sigma C_n \tau_n)$									
			n_0	n_0+1	n_0+2	n_0+3	n_0+4	n_0+5	n_0+6	n_0+7	n_0+8	n_0+9
1	3P 0	8	0.587180	-0.163257	-0.257731							
2	1S 0	8	-0.344826	0.279204	-0.718884							
3	3P 1	7	-0.499999	-0.371229	-0.717952	-0.076303	-0.603022					
4	3P 2	4	-0.509434	0.233106	0.442135	0.541047	0.328013	0.108779	-0.029126	-0.498529	-0.58239	0.357197
5	3F 2	5	-0.229022	0.627656	-0.306934	0.271460	-0.468068	-0.302576	0.609148	-0.006448	0.224254	
6	1D 2	6	0.074418	0.302448	0.349665	-0.122113	-0.465897	-0.046832	-0.633816	-0.255465		
7	3F 3	7	0.062675	-0.024218	-0.670869	-0.301113	-0.664346	0.634568	-0.059419			
8	3F 4	8	0.721884	-0.406932	0.158103	-0.403569	-0.961316	-0.792554				
9	3H 4	9	0.454544	-0.071044	-0.780496	-0.372530	0.622526					
10	1G 4	10	1.068679	-0.082951	0.308624	-1.268054						
11	3H 5	11	0.683293	-0.542705	0.050817							
12	3H 6	12	0.937480	-0.222381								
13	11 6	13	-1.416631									

TABLE XV. Tm^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S')) || \Sigma C_6 || J(LS))$

n'	$\gamma_{n'}$	n_0	$(\gamma_{n'} \Sigma C_6 \gamma_n)$						
			n_0	n_0+1	n_0+2	n_0+3	n_0+4	n_0+5	n_0+6
1	3P 0	12	-0.351265	-0.172700					
2	1S 0	12	0.015921	0.946299					
3	3P 1	11	0.381690	0.449655	-0.042104				
4	3P 2	8	-0.008344	-0.099162	-0.415045	-0.553503	-0.190825	-1.071767	
5	3F 2	8	-0.264944	-0.359633	-0.258090	0.979178	-0.648925	-0.743873	
6	1D 2	8	0.192071	-0.609645	-0.037426	0.163173	-0.389119	1.169055	
7	3F 3	7	0.319345	0.527810	-0.681971	-0.699555	-0.000000	1.171510	-0.109696
8	3F 4	8	0.662111	-0.579100	0.343265	-1.230376	-0.623448	0.794383	
9	3H 4	9	0.975570	-0.776527	0.123402	-0.985090	-0.398150		
10	1G 4	10	0.916926	0.934876	0.142744	1.020011			
11	3H 5	11	-0.445123	1.020578	-0.095563				
12	3H 6	12	-1.124712	0.147959					
13	1I 6	13	0.441572						

$$\langle J'M'(L'S'\omega') | H | JM(LS\omega) \rangle = \delta_{JJ'} \delta_{MM'} \delta_{(L'S'\omega'), (LS\omega)} E(J(LS\omega)) ; \quad (17)$$

and (4) vary the B_{km} and centroids, $E(J(LS\omega))$, to obtain a least squares fit with experimental levels. Within the approximation of constant basis wave functions, this procedure is tantamount to a simultaneous diagonalization of $H + H^x$ since, by Wong's method, the "free-ion" Hamiltonian may be inferred from the resultant centroids, and the crystal field Hamiltonian is determined by the resultant B_{km} .

TABLE XVI. Nd^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S'w') || \Sigma C_2 || J(LS_w))$

n'	$J' n'$	n_0	$n =$										n_0
			n_0	n_0+1	n_0+2	n_0+3	n_0+4	n_0+5	n_0+6	n_0+7			
1	4S 3/2	1	0.032836	-0.026214	0.005950	0.039986	-0.007244	-0.063317	-0.039054				
2	4F 3/2	2	0.339661	-0.385166	-0.949571	0.110770	0.428746	0.390132					
3	4F 5/2	3	0.287851	-0.707504	-0.354338	-0.664543	-0.707220	0.142775	0.042483	-0.110086			
4	4G 5/2	4	0.075427	0.269469	0.004553	0.021759	-0.068006	1.294736	0.042697				
5	4F 7/2	5	0.524794	-0.553996	-0.511694	-0.421464	-0.043049	0.104467	-0.033328	-0.251660			
6	4G 7/2	6	0.448902	-0.328195	0.032171	0.320949	0.310972	1.083151	-0.054476				
7	2G 7/2 (1)	7	0.124433	0.221964	0.375500	-0.119439	0.906681	0.111158					
8	4F 9/2	8	0.510183	0.040488	0.299347	-0.015969	0.408135	0.081228					
9	4I 9/2	9	-0.473344	-0.131237	0.190513	0.010183	-0.011184						
10	2H 9/2 (2)	10	0.459275	-0.072154	0.355319	-0.268724							
11	4I 11/2	11	-0.496846	-0.089470	0.218747	-0.008758							
12	2H 11/2 (2)	12	0.142776	-0.091398	-0.494615								
13	4I 13/2	13	-0.562442	0.191108									
14	4I 15/2	14	-0.660762										

TABLE XVII. Nd^{3+} REDUCED MATRIX ELEMENTS $\langle J'(L'S')\omega' | | \sum C_4 | | J(LS\omega) \rangle$

n'	$\tau_{n'}$	$n =$										
		n_0	n_0+1	n_0+2	n_0+3	n_0+4	n_0+5	n_0+6	n_0+7	n_0+8	n_0+9	n_0+10
1	4s 3/2	3	-0.027556	-0.174735	0.024037	-0.495936	-0.325212	-0.058060	-0.058540	0.074617	0.006332	0.268860
2	4f 3/2	3	0.258154	-0.237622	-0.317635	0.272881	0.238718	0.078336	0.540335	0.135311	-0.425425	0.015378
3	4f 5/2	3	0.163216	-0.405531	0.263965	-0.043020	0.093512	-0.253355	0.549380	-0.200100	0.462519	0.061157
4	4g 5/2	4	0.493774	0.360100	-0.535072	-0.435172	-0.090004	0.721761	-0.132377	-0.606808	0.019780	0.210885
5	4f 7/2	5	0.098475	-0.292687	-0.287962	0.343743	0.231893	0.208535	0.549383	-0.143407	0.646444	-0.443605
6	4g 7/2	6	0.244690	-0.026020	0.106536	0.447771	0.253172	0.350097	-0.162776	-0.540547	0.185414	
7	2g 7/2 (1)	7	-0.012113	0.257213	0.484703	0.195826	0.484313	-0.006925	-0.360249	0.046662		
8	4f 9/2	8	-0.357564	0.108470	-0.057823	0.209565	0.177674	0.527782	0.798536			
9	4i 9/2	9	-0.469816	-0.100919	0.369643	0.058298	-0.131416	0.004105				
10	2h 9/2 (2)	10	0.045811	0.022195	0.070246	0.088044	0.519339					
11	4i 11/2	11	-0.384327	-0.108727	0.414927	-0.118018						
12	2h 11/2 (2)	12	-0.041504	-0.147838	-0.297266							
13	4i 13/2	13	-0.469221	0.388905								
14	4i 15/2	14	-0.487946									

TABLE XVIII. Nd^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S'\omega') || \sum C_6 || J(LS\omega))$

n'	$J_{n'}$	n_0	$(J' \sum C_6 J_n)$									
			n_0	n_0+1	n_0+2	n_0+3	n_0+4	n_0+5	n_0+6	n_0+7	n_0+8	n_0+9
1	4s 3/2	8	0.046623	0.619603	-0.019383	0.582979	-0.052899	0.734585	0.733994			
2	4f 3/2	8	-0.430755	-0.299254	-0.188123	0.818233	-0.115150	-0.583199	0.216631			
3	4f 5/2	5	0.383562	0.428742	0.366592	0.420304	-0.804918	0.090337	0.243854	0.195979	0.810306	-0.613764
4	4g 5/2	5	0.516628	0.287106	0.377538	-0.467405	0.242037	-0.053441	-0.397527	-0.154512	0.277457	-0.084173
5	4f 7/2	5	-0.411985	0.070962	-0.123917	-0.352169	-0.832544	-0.076940	-0.710437	-0.454932	0.012953	1.005682
6	4g 7/2	6	0.336965	0.247842	0.110768	0.300511	0.796861	0.139438	-0.435347	-0.307016	0.067170	
7	2g 7/2 (1)	7	0.196500	0.664218	0.225750	-0.546193	-0.281440	0.752395	-0.249594	0.413896		
8	4f 9/2	8	-0.029358	-0.260513	0.060935	-0.774801	0.176239	-0.917710	-0.872591			
9	4i 9/2	9	-1.062671	-0.434186	1.378836	0.129929	-0.862461	0.271728				
10	2h 9/2 (2)	10	0.667681	-0.200510	0.667282	-0.434152	-0.353281					
11	4i 11/2	11	-0.331779	-0.101115	1.421068	-0.826117						
12	2h 11/2 (2)	12	-0.217820	0.067921	-0.005544							
13	4i 13/2	13	-0.616629	1.538633								
14	4i 15/2	14	-1.775096									

TABLE XIX. Er^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S'\omega')) || \Sigma C_2 || J(LS\omega)$

n'	$\psi_{n'}$	n_o	$(\psi_{n'} \Sigma C_2 \psi_n)$				
			n_o	n_o+1	n_o+2	n_o+3	n_o+4
1	4S 3/2	1	-0.262482	0.220321	-0.123648	0.010977	
2	4F 3/2	2	-0.358546	0.339569	-0.072840		
3	4F 5/2	3	-0.166956	0.377745	-0.027622	-0.141576	
4	4F 7/2	4	-0.531058	0.150517	0.174346	-0.081189	-0.478841
5	4F 9/2	5	-0.478750	-0.488599	0.362506	0.823042	0.137362
6	4I 9/2	6	0.059525	0.074883	0.622563	0.027990	
7	4I11/2	7	0.380479	-0.258171	-0.248614	-0.229408	
8	2H11/2 (2)	8	0.064755	-0.207437	-1.153236		
9	4I13/2	9	0.567533	-0.190782			
10	4I15/2	10	0.679091				

TABLE XX. Er^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S'\omega')) || \Sigma C_4 || J(LS\omega)$

n'	$\psi_{n'}$	n_o	$(\psi_{n'} \Sigma C_4 \psi_n)$					
			n_o	n_o+1	n_o+2	n_o+3	n_o+4	n_o+5
1	4S 3/2	3	0.071178	-0.085995	-0.020083	0.316716	0.073430	0.503102
2	4F 3/2	3	-0.211138	0.272688	0.071543	-0.540948	0.343382	0.024375
3	4F 5/2	3	-0.079428	-0.252989	0.554343	-0.270880	-0.352943	0.273028
4	4F 7/2	4	-0.110153	-0.208608	-0.348339	-0.580590	-0.139612	-0.655039
5	4F 9/2	5	0.318566	-0.086966	0.119105	0.168638	-0.441658	-0.825465
6	4I 9/2	6	0.313221	-0.292901	0.290134	-0.116014	-0.469588	
7	4I11/2	7	0.213348	-0.419460	-0.466250	-0.019705		
8	2H11/2 (2)	8	-0.296091	-0.278804	-0.724416			
9	4I13/2	9	0.469379	-0.386437				
10	4I15/2	10	0.696071					

TABLE XXI. Er^{3+} REDUCED MATRIX ELEMENTS $(J'(L'S'\omega') || \Sigma C_6 || J(LS\omega))$

n'	$\psi_{n'}$	n_0	$n =$ $(\psi_{n'} \Sigma C_6 \psi_n)$						
			n_0	n_0+1	n_0+2	n_0+3	n_0+4	n_0+5	n_0+6
1	4S 3/2	5	0.207436	-0.644214	-0.347284	0.128523	-0.751733	-0.600759	
2	4F 3/2	5	0.311537	0.301793	-0.890596	0.069566	0.237355	-0.455555	
3	4F 5/2	4	-0.406985	-0.763623	0.407966	-0.066968	0.545644	-0.748047	0.603501
4	4F 7/2	4	0.403600	-0.156917	0.835497	0.497156	-0.809732	-0.014258	-1.011190
5	4F 9/2	5	-0.276963	-0.213917	1.447424	-0.059624	0.341243	0.867992	
6	4I 9/2	6	1.129530	-0.455469	0.682982	1.081023	0.127155		
7	4I 11/2	7	0.211155	-0.245872	-1.331432	0.803101			
8	2H 11/2 (2)	8	0.419948	0.293424	-0.388420				
9	4I 13/2	9	0.611945	-1.528391					
10	4I 15/2	10	1.741019						

LITERATURE CITED

- (1) J. Sugar, Phys. Rev. Lett., 14 (1965), 731.
- (2) N. Spector and J. Sugar, J. Opt. Soc. Am., 66 (1976), 436.
- (3) V. Kaufman and J. Sugar, J. Opt. Soc. Am., 66 (1976) 439.
- (4) W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys., 49 (1968), 4412-55.
- (5) K. Rajnak and B. G. Wybourne, Phys. Rev., 132 (1963), 280.
- (6) B. G. Wybourne, Spectroscopic Properties of Rare Earths, Interscience Publishers, New York (1965).
- (7) J. S. Margolis, J. Chem. Phys., 35 (1961) 1370.
- (8) N. Karayianis, D. E. Wortman, and H. P. Jenssen, J. Phys. Chem. Solids, 37 (1976), 676.
- (9) P. Grunberg, S. Hufner, E. Orlich, and J. Schmidt, Phys. Rev., 184 (1969), 290.
- (10) E. Y. Wong, J. Chem. Phys., 35 (1961), 544.
- (11) N. Karayianis and C. A. Morrison, Rare Earth Ion-Host Crystal Interactions. 2. Local Distortion and Other Effects in Reconciling Lattice Sums and Phenomenological B_{km} , Harry Diamond Laboratories TR-1682 (January 1975), table II.
- (12) E. Merzbacher, Quantum Mechanics, John Wiley and Sons, Inc., New York (1961), 396.
- (13) C. W. Nielson and G. F. Koster, Spectroscopic Coefficients for the p^N , d^N , and f^N Configurations, The MIT Press, Cambridge, MA (1963).
- (14) M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, The 3-j and 6-j Symbols, Technology Press, Cambridge, MA (1959).
- (15) B. R. Judd, Operator Techniques in Atomic Spectroscopy, McGraw-Hill Book Co., Inc., New York (1963), 166-192.
- (16) Donald E. Wortman, Clyde A. Morrison, and Nick Karayianis, Rare Earth Ion-Host Lattice Interactions. 5. Lanthanides in $CaWO_4$, Harry Diamond Laboratories TR-1794 (June 1977).

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